

CAS ONLINE PRINTOUT

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(FILE 'HOME' ENTERED AT 09:54:51 ON 13 SEP 2002)

FILE 'CAPLUS' ENTERED AT 09:55:02 ON 13 SEP 2002

L1 5225 S ARYLATION
L2 120683 S TRANSITION METAL
L3 147745 S TRANSITION METAL#
L4 226062 S LIGAND
L5 27 S L3 AND L4 AND L1
L6 544026 S BASE
L7 8 S L6 AND L5

=> D BIB ABS KWIC 1-8

L7 ANSWER 1 OF 8 CAPLUS COPYRIGHT 2002 ACS
AN 2001:366737 CAPLUS

DN 134:366672

TI Transition metal-catalyzed process for preparing
n-aryl amine compounds

IN Hartwig, John F.; Hamann, Blake C.

PA Yale University, USA

SO U.S., 10 pp.
CODEN: USXXAM

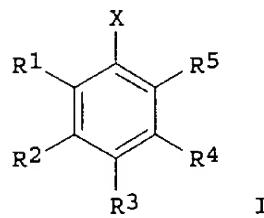
DT Patent

LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 6235938	B1	20010522	US 1999-329474	19990610
OS	CASREACT 134:366672; MARPAT 134:366672				

GI



AB The title process involves reacting a compd. having an amino group with an arylating compd., esp. an aryl chloride and or tosylate, in the presence of a base and a transition metal catalyst, consisting of a Group 8 metal and at least one chelating bisphosphine ligand contg. at least one sterically hindered alkyl substituent, under reaction conditions effective to form an N-arylamine (I) [wherein X = halo or S-contg. leaving group; R1-R5 = independently H, CN, alkyl, alkoxy, vinyl, alkenyl, formyl, CF₃, CC₁₃, halo, Ph, amide, acyl, ester, amino, thioalkoxy, phosphino, etc.]. The method uses readily available starting materials, is efficient, and avoids harsh reaction conditions. For example, PhNH₂ was added to a vial contg. 4-chlorotoluene, Pd(dba)₂, (R)-(-)-1-[(S)-2-(dicyclohexylphosphino)ferrocenyl]ethyldicyclohexylphosphine, and NaOBu-t in PhMe in a dry box and the sealed vial heated in a 110.degree.C oil bath for 16 h to give N-phenyl-4-toluidine (99%).

RE.CNT 4 THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS RECORD

CAS ONLINE PRINTOUT

ALL CITATIONS AVAILABLE IN THE RE FORMAT

TI **Transition metal-catalyzed process for preparing n-aryl amine compounds**

AB The title process involves reacting a compd. having an amino group with an arylating compd., esp. an aryl chloride and or tosylate, in the presence of a **base** and a **transition metal catalyst**, consisting of a Group 8 metal and at least one chelating bisphosphine **ligand** contg. at least one sterically hindered alkyl substituent, under reaction conditions effective to form an N-arylamine (I) [wherein X = halo or S-contg. leaving group; R1-R5 = independently H, CN, alkyl, alkoxy, vinyl, alkenyl, formyl, CF3, CC13, halo, Ph, amide, acyl, ester, amino, thioalkoxy, phosphino, etc.]. The method uses readily available starting materials, is efficient, and avoids harsh reaction conditions. For example, PhNH2 was added to a vial contg. 4-chlorotoluene, Pd(dba)2, (R)-(-)-1-[(S)-2-(dicyclohexylphosphino)ferrocenyl]ethyldicyclohexylphosphine, and NaOBu-t in PhMe in a dry box and the sealed vial heated in a 110.degree.C oil bath for 16 h to give N-phenyl-4-toluidine (99%).

ST arylamine prepn **transition metal phosphine ligand catalyst; arylation amine**

IT Amines, preparation
RL: IMF (Industrial manufacture); PUR (Purification or recovery); SPN (Synthetic preparation); PREP (Preparation)
(aryl, secondary; prepn. of N-arylamines by **arylation** of amines with aryl halides or tosylates using catalysts comprising Group 8 metals and chelating bisphosphine ligands)

IT **Arylation**
Arylation catalysts
(prep. of N-arylamines by **arylation** of amines with aryl halides or tosylates using catalysts comprising Group 8 metals and chelating bisphosphine ligands)

IT **Aryl halides**
RL: RCT (Reactant); RACT (Reactant or reagent)
(prep. of N-arylamines by **arylation** of amines with aryl halides or tosylates using catalysts comprising Group 8 metals and chelating bisphosphine ligands)

IT Amines, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(primary; prepn. of N-arylamines by **arylation** of amines with aryl halides or tosylates using catalysts comprising Group 8 metals and chelating bisphosphine ligands)

IT 3375-31-3, Palladium diacetate 32005-36-0, Bis(dibenzylideneacetonato)palladium 84680-95-5 158923-07-0, (R)-(-)-1-[(S)-2-(Dicyclohexylphosphino)ferrocenyl]ethyldicyclohexylphosphine 158923-11-6, (R)-(-)-1-[(S)-2-(Dicyclohexylphosphino)ferrocenyl]ethyldi-*t*-butylphosphine
RL: CAT (Catalyst use); USES (Uses)
(catalyst component; prepn. of N-arylamines by **arylation** of amines with aryl halides or tosylates using catalysts comprising Group 8 metals and chelating bisphosphine ligands)

IT 31144-33-9P, N,N-Dibutyl-4-methylaniline
RL: SPN (Synthetic preparation); PREP (Preparation)
(prep. of N-arylamines by **arylation** of amines with aryl halides or tosylates using catalysts comprising Group 8 metals and chelating bisphosphine ligands)

IT 620-84-8P 7277-86-3P, N-Butyl-2-methylaniline 10387-24-3P,
N-Butyl-4-methylaniline 31053-03-9P, 1-(4-Methylphenyl)piperidine 32040-09-8P 36602-01-4P, 4-Cyanodiphenylamine 41115-19-9P,
N-Butyl-2,4-dimethylaniline 56506-60-6P, N-Hexyl-4-methylaniline 78888-05-8P, 4-Butyldiphenylamine 167864-23-5P, N-Butyl-4-butylaniline
RL: IMF (Industrial manufacture); PUR (Purification or recovery); SPN (Synthetic preparation); PREP (Preparation)
(product; prepn. of N-arylamines by **arylation** of amines with

CAS ONLINE PRINTOUT

aryl halides or tosylates using catalysts comprising Group 8 metals and chelating bisphosphine ligands)

IT 62-53-3, Aniline, reactions 95-49-8, 2-Chlorotoluene 106-38-7, 4-Bromotoluene 106-43-4, 4-Chlorotoluene 109-73-9, Butylamine, reactions 110-89-4, Piperidine, reactions 110-91-8, Morpholine, reactions 111-26-2, Hexylamine 2845-89-8, 3-Chloroanisole 4214-28-2, 4-Iodo-m-xylene 20651-67-6, 4-Iodobutylbenzene 36800-95-0, 4-Cyanophenyltosylate

RL: RCT (Reactant); RACT (Reactant or reagent)
(reactant; prepn. of N-arylamines by arylation of amines with aryl halides or tosylates using catalysts comprising Group 8 metals and chelating bisphosphine ligands)

L7 ANSWER 2 OF 8 CAPLUS COPYRIGHT 2002 ACS

AN 2001:12419 CAPLUS

DN 134:86044

TI Preparation of chiral 2-amino-2'-diphenylphosphino-1,1'-binaphthyl derivatives as metal catalyst ligands

IN Zhang, Xumu

PA The Penn State Research Foundation, USA

SO PCT Int. Appl., 93 pp.

CODEN: PIXXD2

DT Patent

LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	WO 2001000581	A1	20010104	WO 2000-US17903	20000629
	W: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM				
	RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG				
	US 6380392	B1	20020430	US 2000-607005	20000629

PRAI US 1999-141795P P 19990630

OS CASREACT 134:86044; MARPAT 134:86044

AB Title ligands are bidentate, tridentate, tetridentate, or pentadentate and include P-P, P-N, N-N, mixed P-N, Schiff base or carbene sites.

Transition metal complexes with these ligands are effective catalysts for asym. reactions. Thus, Et₂Zn addn. to 2-cyclohexenone in the presence of (S)-2-(2-pyridinylcarbonylamino)-2'-diphenylphosphino-1,1'-binaphthyl complex with Cu gave (S)-3-ethylcyclohexanone of 92% ee with 98% conversion.

RE.CNT 4 THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS RECORD

ALL CITATIONS AVAILABLE IN THE RE FORMAT

AB Title ligands are bidentate, tridentate, tetridentate, or pentadentate and include P-P, P-N, N-N, mixed P-N, Schiff base or carbene sites.

Transition metal complexes with these ligands are effective catalysts for asym. reactions. Thus, Et₂Zn addn. to 2-cyclohexenone in the presence of (S)-2-(2-pyridinylcarbonylamino)-2'-diphenylphosphino-1,1'-binaphthyl complex with Cu gave (S)-3-ethylcyclohexanone of 92% ee with 98% conversion.

ST aminodiphenylphosphinobinaphthyl deriv chiral prepn catalyst ligand; asym reaction catalyst aminodiphenylphosphinobinaphthyl deriv chiral prepn

IT Arylation catalysts
(Heck, asym.; prepn. of chiral 2-amino-2'-diphenylphosphino-1,1'-binaphthyl derivs. as metal catalyst ligands)

CAS ONLINE PRINTOUT

L7 ANSWER 3 OF 8 CAPLUS COPYRIGHT 2002 ACS
AN 2000:547497 CAPLUS
DN 133:150343
TI Transition metal-catalyzed process for preparing arylamines
IN Hartwig, John F.; Kawatsura, Motoi; Hauck, Sheila I.; Shaughnessy, Kevin H.; Alcazar-Roman, Luis M.
PA Yale University, USA
SO U.S., 14 pp., Cont.-in-part of U.S. 5,977,361.
CODEN: USXXAM

DT Patent

LA English

FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 6100398	A	20000808	US 1999-343383	19990630
	US 5977361	A	19991102	US 1998-172497	19981014
PRAI	US 1997-62211P	P	19971016		
	US 1998-172497	A2	19981014		

OS CASREACT 133:150343; MARPAT 133:150343

AB The title process for comprises reaction of an amine with an arylating agent in the presence of a **base** and a catalyst comprising a Group 8 metal and P(CMe₃)₃ as a **ligand**. Thus, Ph₂NH and PhBr were maintained 1h at room temp. in a dry box in PhMe contg. Pd(dba)₂ and P(CMe₃)₃ to give 91% Ph₃N.

RE.CNT 15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

TI Transition metal-catalyzed process for preparing arylamines

AB The title process for comprises reaction of an amine with an arylating agent in the presence of a **base** and a catalyst comprising a Group 8 metal and P(CMe₃)₃ as a **ligand**. Thus, Ph₂NH and PhBr were maintained 1h at room temp. in a dry box in PhMe contg. Pd(dba)₂ and P(CMe₃)₃ to give 91% Ph₃N.

ST arylamine prepn catalyst; N arylation catalyst

IT Amines, preparation

RL: IMF (Industrial manufacture); PUR (Purification or recovery); SPN (Synthetic preparation); PREP (Preparation)
(arom., secondary; transition metal-catalyzed process for prep. arylamines)

IT Amines, preparation

RL: IMF (Industrial manufacture); PUR (Purification or recovery); SPN (Synthetic preparation); PREP (Preparation)
(arom., tertiary; transition metal-catalyzed process for prep. arylamines)

IT Amines, preparation

RL: IMF (Industrial manufacture); PUR (Purification or recovery); SPN (Synthetic preparation); PREP (Preparation)
(arom.; transition metal-catalyzed process for prep. arylamines)

IT Arylation

Arylation catalysts
(transition metal-catalyzed process for prep. arylamines)

IT 122-39-4P, Diphenylamine, preparation 603-34-9P 827-60-1P,
1-(4-Methylphenyl)-1H-pyrrole 4316-51-2P, N,N-Diphenyl-4-methoxyaniline
4316-55-6P, N,N-Diphenyl-2-methylbenzenamine 7178-40-7P,
4-(2-Methylphenyl)morpholine 10387-24-3P, N-Butyl-4-methylbenzenamine
13050-56-1P, Tris(4-methoxyphenyl)amine 14118-16-2P,
N,N,N',N'-Tetraphenyl-p-phenylenediamine 17425-20-6P, Butyl
4-methylphenylcarbamate 20441-00-3P, 4-Diphenylaminobenzonitrile

CAS ONLINE PRINTOUT

31144-33-9P, N,N-Dibutyl-4-methylbenzenamine 74965-31-4P, Butyl
 2-methylphenylcarbamate 82749-64-2P, N,N-Dibutyl-2-methylbenzenamine
 91644-88-1P, Butyl 4-methoxyphenylcarbamate 93597-01-4P,
 1-(4-Methoxyphenyl)-1H-indole 119896-38-7P, 4-
 Methylphenylaminobenzonitrile 138900-23-9P, 5-Methoxy-1-(4-fluorophenyl)-
 1H-indole 167283-32-1P, 1-(4-Methylphenyl)1H-indole 240408-60-0P,
 3-Methyl-1-(2-methylphenyl)-1H-indole 287476-96-4P
 RL: IMF (Industrial manufacture); PUR (Purification or recovery); SPN
 (Synthetic preparation); PREP (Preparation)
 (transition metal-catalyzed process for prep.
 arylamines)

IT 62-53-3, Benzenamine, reactions 83-34-1, 3-Methyl-1H-indole 95-46-5,
 2-Bromotoluene 100-61-8, N-Methylaniline, reactions 101-70-2,
 Bis(4-methoxyphenyl)amine 104-92-7, 4-Bromoanisole 106-37-6,
 p-Dibromobenzene 106-43-4, p-Chlorotoluene 108-86-1, Bromobenzene,
 reactions 108-90-7, Chlorobenzene, reactions 109-97-7, 1H-Pyrrole
 110-91-8, Morpholine, reactions 111-92-2, Dibutylamine 120-72-9,
 1H-Indole, reactions 460-00-4, 4-Bromo-1-fluorobenzene 623-00-7,
 4-Bromobenzonitrile 623-03-0, 4-Chlorobenzonitrile 623-12-1,
 4-Chloroanisole 1006-94-6, 5-Methoxy-1H-indole
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (transition metal-catalyzed process for prep.
 arylamines)

L7 ANSWER 4 OF 8 CAPLUS COPYRIGHT 2002 ACS
 AN 2000:381474 CAPLUS

DN 133:30376

TI Carbonyl arylations and vinylations using **transition**
metal catalysts

IN Kawatsura, Motoi; Hartwig, John F.

PA Yale University, USA

SO U.S., 12 pp.

CODEN: USXXAM

DT Patent

LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 6072073	A	20000606	US 1999-376898	19990818
PRAI	US 1998-97472P	P	19980821		

OS CASREACT 133:30376; MARPAT 133:30376

AB The invention is directed to a process for prep. an .alpha.-arylated or
 vinylated carbonyl-contg. compds., comprising reacting a compd. having a
 carbonyl group with an arylating or vinylating compd. in the presence of a
 base and a **transition metal catalyst**. The
transition metal catalyst has the formula $X_nM(E R_1-4)^m$ [X
 is an optional ligand, M is a Group 8 transition
 metal, E is an element bearing a nonbonding electron pair when E
 is not bonded to the metal, and R is a substituent bonded to E through a
 carbon, nitrogen, oxygen, or sulfur atom, with the proviso that R3 cannot
 contain 3 aryl groups, n is an integer from 0 to 4, and m is an integer
 from 1-4]. E.g., BrPh and acetophenone were added to a mixt. of $Pd(OAc)_2$,
 $(Me_3C)_3P$, and $NaOCCMe_3$ in THF to give 96% 1,2-diphenyl-1-ethanone.

RE.CNT 1 THERE ARE 1 CITED REFERENCES AVAILABLE FOR THIS RECORD
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

TI Carbonyl arylations and vinylations using **transition**
metal catalysts

AB The invention is directed to a process for prep. an .alpha.-arylated or
 vinylated carbonyl-contg. compds., comprising reacting a compd. having a
 carbonyl group with an arylating or vinylating compd. in the presence of a
 base and a **transition metal catalyst**. The
transition metal catalyst has the formula $X_nM(E R_1-4)^m$ [X

CAS ONLINE PRINTOUT

is an optional ligand, M is a Group 8 transition metal, E is an element bearing a nonbonding electron pair when E is not bonded to the metal, and R is a substituent bonded to E through a carbon, nitrogen, oxygen, or sulfur atom, with the proviso that R3 cannot contain 3 aryl groups, n is an integer from 0 to 4, and m is an integer from 1-4]. E.g., BrPh and acetophenone were added to a mixt. of Pd(OAc)₂, (Me₃C)₃P, and NaOCMe₃ in THF to give 96% 1,2-diphenyl-1-ethanone.

ST carbonyl arylation vinylation transition metal catalyst

IT **Arylation**

Arylation catalysts

Vinylation

Vinylation catalysts

 (arylations and vinylations of carbonyl compds. catalyzed by transition metal compds.)

IT **Transition metal compounds**

RL: CAT (Catalyst use); USES (Uses)

 (arylations and vinylations of carbonyl compds. catalyzed by transition metal compds.)

IT **Carbonyl compounds (organic), reactions**

RL: RCT (Reactant); RACT (Reactant or reagent)

 (arylations and vinylations of carbonyl compds. catalyzed by transition metal compds.)

IT 1608-26-0, Tris(dimethylamino)phosphine 1636-14-2 2283-11-6, Tris(diethylamino)phosphine 2622-14-2, Tricyclohexylphosphine 3375-31-3, Palladium diacetate 13716-12-6, Tri-tert-butylphosphine 32005-36-0, Bis(dibenzylideneacetone)palladium 40358-68-7 42964-60-3 65768-04-9 83356-93-8 93713-88-3 107531-50-0 120666-13-9 134484-36-9 139190-38-8 145964-33-6 252288-04-3

RL: CAT (Catalyst use); USES (Uses)

 (arylations and vinylations of carbonyl compds. catalyzed by transition metal compds.)

IT 83-13-6P, Diethyl phenylmalonate 451-40-1P 951-85-9P 1444-65-1P 2042-85-5P 13740-70-0P 56705-50-1P 58751-83-0P 84839-92-9P 113279-72-4P, Di-tert-butyl phenylmalonate 221662-40-4P 273381-75-2P 273381-76-3P

RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP (Preparation)

 (arylations and vinylations of carbonyl compds. catalyzed by transition metal compds.)

IT 90-90-4, 4-Bromobenzophenone 93-55-0, Ethyl phenyl ketone 98-86-2, Methyl phenyl ketone, reactions 105-53-3, Diethyl malonate 108-86-1, Bromobenzene, reactions 108-90-7, Chlorobenzene, reactions 108-94-1, Cyclohexanone, reactions 134-85-0, 4-Chlorobenzophenone 541-16-2, Di-tert-butyl malonate 563-80-4, Isopropyl methyl ketone 565-69-5, Ethyl isopropyl ketone 611-70-1, Isopropyl phenyl ketone 623-12-1, 4-Chloroanisole 1590-08-5, 2-Methyl-1-tetralone 2398-37-0, 3-Bromoanisole 2845-89-8, 3-Chloroanisole 3899-96-5

RL: RCT (Reactant); RACT (Reactant or reagent)

 (arylations and vinylations of carbonyl compds. catalyzed by transition metal compds.)

L7 ANSWER 5 OF 8 CAPLUS COPYRIGHT 2002 ACS

AN 2000:289079 CAPLUS

DN 132:293568

TI **Transition metal-catalyzed preparation of .alpha.-arylated carbonyl compounds.**

IN Hartwig, John F.; Hamann, Blake C.

PA Yale University, USA

SO U.S., 9 pp.

CODEN: USXXAM

DT Patent

CAS ONLINE PRINTOUT

LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 6057456	A	20000502	US 1998-173527	19981015
PRAI	US 1997-62212P	P	19971016		
OS	CASREACT 132:293568; MARPAT 132:293568				
AB	<p>.alpha.-Arylated carbonyl compds. were prep'd. by reacting a compd. having .gtreq.1 CO group with an arylating compd. in the presence of a base and a catalyst comprising a group 8 transition metal and a chelating ligand selected from unsatd. Group 15 element contg. heterocycles, metallocenes, alkanes, and arylenes. Thus, PhBr, AcPh, Pd(dibenzylideneacetone)2, 1,1'-bis(di-O- tolylphosphino)ferrocene, and KN(SiMe)2 were stirred at 70.degree. for 2 h in THF to give 84% PhCH2COPh.</p>				

RE.CNT 13 THERE ARE 13 CITED REFERENCES AVAILABLE FOR THIS RECORD
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

TI **Transition metal-catalyzed preparation of**
 .alpha.-arylated carbonyl compounds.

AB .alpha.-Arylated carbonyl compds. were prep'd. by reacting a compd. having
 .gtreq.1 CO group with an arylating compd. in the presence of a
base and a catalyst comprising a group 8 **transition**
metal and a chelating **ligand** selected from unsatd. Group
 15 element contg. heterocycles, metallocenes, alkanes, and arylenes.
 Thus, PhBr, AcPh, Pd(dibenzylideneacetone)2, 1,1'-bis(di-O-
 tolylphosphino)ferrocene, and KN(SiMe)2 were stirred at 70.degree. for 2 h
 in THF to give 84% PhCH2COPh.

ST arom ketone prep'n; aryl halide ketone coupling **transition**
metal catalyst

IT **Arylation catalysts**
 (Group 8 metals with Group 15-contg. ligands; **transition**
metal-catalyzed prep'n. of .alpha.-arylated carbonyl compds.)

IT Ketones, preparation
 RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP
 (Preparation)
 (arom.; **transition metal-catalyzed prep'n.** of
 .alpha.-arylated carbonyl compds.)

IT **Arylation**
 (**transition metal-catalyzed prep'n.** of
 .alpha.-arylated carbonyl compds.)

IT Group VIII elements
 RL: CAT (Catalyst use); USES (Uses)
 (**transition metal-catalyzed prep'n.** of
 .alpha.-arylated carbonyl compds.)

IT 538-58-9 3375-31-3, Palladium diacetate 12150-46-8 32005-36-0
 54792-65-3 72287-26-4 73881-42-2 98327-87-8, BINAP 153305-67-0
 247921-86-4 264284-69-7 264919-16-6 264919-17-7 264919-18-8
 264919-19-9 264919-20-2
 RL: CAT (Catalyst use); USES (Uses)
 (**transition metal-catalyzed prep'n.** of
 .alpha.-arylated carbonyl compds.)

IT 451-40-1P 2042-85-5P 5033-67-0P 6721-67-1P 10474-32-5P
 13196-28-6P 13740-70-0P 24845-40-7P 27798-41-0P 62043-83-8P
 86607-65-0P 93304-03-1P 144601-61-6P 264284-68-6P
 RL: IMF (Industrial manufacture); SPN (Synthetic preparation); PREP
 (Preparation)
 (**transition metal-catalyzed prep'n.** of
 .alpha.-arylated carbonyl compds.)

IT 75-97-8 88-15-3 93-55-0, Propiophenone 95-46-5, 2-Bromotoluene
 98-86-2, Acetophenone, reactions 104-92-7, 4-Methoxybromobenzene
 108-86-1, Bromobenzene, reactions 591-50-4, Iodobenzene 611-70-1
 932-16-1 1118-71-4 1192-62-7 3972-65-4, 4-Bromo-tert-butylbenzene

CAS ONLINE PRINTOUT

6952-59-6 17496-14-9, 2-Methylindan-1-one 41492-05-1,
 4-Butylbromobenzene
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (transition metal-catalyzed prep. of
 .alpha.-arylated carbonyl compds.)

L7 ANSWER 6 OF 8 CAPLUS COPYRIGHT 2002 ACS
 AN 1998:650086 CAPLUS
 DN 129:275692
 TI Metal-catalyzed amination of organic sulfonates to organic amines
 IN Hartwig, John F.; Driver, Michael S.; Louie, Janis; Hamann, Blake
 PA Yale University, USA
 SO U.S., 11 pp.
 CODEN: USXXAM
 DT Patent
 LA English
 FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI US 5817877	A	19981006	US 1997-933658	19970919
OS MARPAT 129:275692				

AB A process of prep. an org. amine having at least one unsatd. group, such as an arylamine, involving contacting an unsatd. org. sulfonate, such as an aryl sulfonate, with a reactant amine, such as an alkyl or aryl amine, in the presence of a **base** and a **transition metal catalyst** under reaction conditions. The **transition metal catalyst** contains a Group 8 metal and a chelating ligand, for example a Group 15-substituted arylene or Group 15-substituted metallocene, such as 1,1'-bis(diphenylphosphino)-2,2'-binaphthyl or 1,1'-bis(diphenylphosphino)ferrocene, resp. The aryl sulfonate can be prepd. from a phenol and sulfonating agent. E.g., treatment of 4-biphenyl triflate with aniline and NaOBu-tert in the presence of bis(dibenzylideneacetone)palladium and 1,1'-bis(diphenylphosphino)ferrocene in toluene gave 99% 4-PhC₆H₄NHPh. Among the approx. 20 compds. similarly prep'd. were 94% 4-MeOC₆H₄NHPh, 95% 2-MeC₆H₄NHPh, 98% N-phenyl-2-naphthylamine, 95% 4-NCC₆H₄NHBu, and 91% 2-morpholinonaphthalene.

AB A process of prep. an org. amine having at least one unsatd. group, such as an arylamine, involving contacting an unsatd. org. sulfonate, such as an aryl sulfonate, with a reactant amine, such as an alkyl or aryl amine, in the presence of a **base** and a **transition metal catalyst** under reaction conditions. The **transition metal catalyst** contains a Group 8 metal and a chelating ligand, for example a Group 15-substituted arylene or Group 15-substituted metallocene, such as 1,1'-bis(diphenylphosphino)-2,2'-binaphthyl or 1,1'-bis(diphenylphosphino)ferrocene, resp. The aryl sulfonate can be prep'd. from a phenol and sulfonating agent. E.g., treatment of 4-biphenyl triflate with aniline and NaOBu-tert in the presence of bis(dibenzylideneacetone)palladium and 1,1'-bis(diphenylphosphino)ferrocene in toluene gave 99% 4-PhC₆H₄NHPh. Among the approx. 20 compds. similarly prep'd. were 94% 4-MeOC₆H₄NHPh, 95% 2-MeC₆H₄NHPh, 98% N-phenyl-2-naphthylamine, 95% 4-NCC₆H₄NHBu, and 91% 2-morpholinonaphthalene.

ST amination triflate; amine org prep; **arylation** aniline; palladium catalyst amination org sulfonate; **transition metal catalyst** amination org sulfonate

IT Amines, preparation
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (arom.; **transition metal-catalyzed** amination of org. sulfonates to org. amines)

IT Amination
 Amination catalysts

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(transition metal-catalyzed amination of org.
sulfonates to org. amines)

IT Sulfonates
RL: RCT (Reactant); RACT (Reactant or reagent)
(triflates; transition metal-catalyzed amination of
org. sulfonates to org. amines)

IT 12150-46-8, 1,1'-Bis(diphenylphosphino)ferrocene 32005-36-0,
Bis(dibenzylideneacetone)palladium 98327-87-8, BINAP
RL: CAT (Catalyst use); USES (Uses)
(transition metal-catalyzed amination of org.
sulfonates to org. amines)

IT 78-81-9, Isobutylamine 100-61-8, reactions 109-73-9, Butylamine,
reactions 110-89-4, Piperidine, reactions 110-91-8, Morpholine,
reactions 3857-83-8, 2-Naphthyl triflate 17763-78-9, 4-Biphenyl triflate
29540-83-8, p-Tolyl triflate 66107-29-7, p-Anisyl triflate
66107-32-2, 4-Cyanophenyl triflate 66107-34-4, o-Tolyl triflate
124643-34-1, 4-Benzoylphenyl triflate
RL: RCT (Reactant); RACT (Reactant or reagent)
(transition metal-catalyzed amination of org.
sulfonates to org. amines)

IT 135-88-6P, 2-Phenylaminonaphthalene 1205-39-6P, 2-Methyldiphenylamine
1208-86-2P, 4-Methoxydiphenylamine 4714-65-2P, 4-Butylaminobenzonitrile
5465-85-0P, 2-Piperidinonaphthalene 7277-86-3P, N-Butyl-2-methylaniline
7508-21-6P, 2-Morpholinonaphthalene 10282-31-2P, 4-(4-
Cyanophenyl)morpholine 20349-66-0P, 4-(Methylphenylamino)benzophenone
31053-03-9P, 1-p-Tolylpiperidine 32228-99-2P, 4-Phenyldiphenylamine
54837-93-3P, N-Isobutyl-4-methylaniline 96372-83-7P,
4-Piperidinobiphenyl 101906-09-6P, 4-Butylaminobiphenyl 180690-25-9P,
4-Butylaminobenzophenone 186831-37-8P, 2-Isobutylaminonaphthalene
213765-79-8P, 4-sec-Butylaminobenzonitrile
RL: SPN (Synthetic preparation); PREP (Preparation)
(transition metal-catalyzed amination of org.
sulfonates to org. amines)

L7 ANSWER 7 OF 8 CAPLUS COPYRIGHT 2002 ACS
AN 1998:6455 CAPLUS
DN 128:22684
TI Palladium-Catalyzed Direct .alpha.-Arylation of Ketones. Rate
Acceleration by Sterically Hindered Chelating Ligands and Reductive
Elimination From a Transition Metal Enolate Complex
AU Hamann, Blake C.; Hartwig, John F.
CS Department of Chemistry, Yale University, New Haven, CT, 06520-8107, USA
SO Journal of the American Chemical Society (1997), 119(50), 12382-12383
CODEN: JACSAT; ISSN: 0002-7863
PB American Chemical Society
DT Journal
LA English
OS CASREACT 128:22684
AB The direct arylation of ketones by reaction of ketone, aryl
halide, base, and a Pd catalyst contg. DPPF [1,1-
bis(diphenylphosphino)ferrocene] or DTPF [1,1-bis(di-o-
tolylphosphino)ferrocene] is reported, along with the direct observation
of an unusual reductive elimination involving a transition
metal enolate complex. Rates are significantly faster for
reactions involving DTPF, and yields are measurably higher. The reaction
is general for alkyl aryl ketones, including heteroaryl ketones, and can
form secondary, tertiary, or quaternary carbons. Although not
investigated in detail, dialkyl ketones also undergo the arylation
chem. The enolate aryl complex that is a presumed intermediate in the
catalytic process was prep'd. by reaction of (DPPF)Pd(p-C6H4-t-Bu)(Br) with
the enolate salt KOCPh(=CH2). The complex is highly reactive, but was
characterized by 1H, 1H(31P), and 31P(1H) NMR techniques which indicate a

CAS ONLINE PRINTOUT

C-bound enolate. The complex underwent reductive elimination at 50.degree. to form 74-87% yield of .alpha.-aryl ketone in less than 1 h.

TI Palladium-Catalyzed Direct .alpha.-Arylation of Ketones. Rate Acceleration by Sterically Hindered Chelating Ligands and Reductive Elimination From a Transition Metal Enolate Complex

AB The direct **arylation** of ketones by reaction of ketone, aryl halide, **base**, and a Pd catalyst contg. DPPF [1,1-bis(diphenylphosphino)ferrocene] or DTPF [1,1-bis(di-o-tolylphosphino)ferrocene] is reported, along with the direct observation of an unusual reductive elimination involving a **transition metal** enolate complex. Rates are significantly faster for reactions involving DTPF, and yields are measurably higher. The reaction is general for alkyl aryl ketones, including heteroaryl ketones, and can form secondary, tertiary, or quaternary carbons. Although not investigated in detail, dialkyl ketones also undergo the **arylation** chem. The enolate aryl complex that is a presumed intermediate in the catalytic process was prep'd. by reaction of (DPPF)Pd(p-C6H4-t-Bu)(Br) with the enolate salt KOCPh(=CH2). The complex is highly reactive, but was characterized by 1H, 1H(31P), and 31P(1H) NMR techniques which indicate a C-bound enolate. The complex underwent reductive elimination at 50.degree. to form 74-87% yield of .alpha.-aryl ketone in less than 1 h.

ST **arylation** ketone aryl halide palladium catalyst; sterically hindered chelating ligand **arylation** catalyst; reductive elimination **transition metal** enolate complex

IT **Transition metal** complexes
RL: CAT (Catalyst use); USES (Uses)
(catalyst component; palladium-catalyzed **arylation** of ketones by aryl halides using sterically hindered chelating ligands)

IT **Arylation**
Arylation catalysts
(palladium-catalyzed **arylation** of ketones by aryl halides using sterically hindered chelating ligands)

IT **Aryl halides**
Ketones, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(reactant; palladium-catalyzed **arylation** of ketones by aryl halides using sterically hindered chelating ligands)

IT **Elimination reaction**
(reductive; palladium-catalyzed **arylation** of ketones by aryl halides using sterically hindered chelating ligands)

IT 12150-46-8, DPPF 15827-60-8, DTPF 32005-36-0
RL: CAT (Catalyst use); USES (Uses)
(catalyst component; palladium-catalyzed **arylation** of ketones by aryl halides using sterically hindered chelating ligands)

IT 185259-33-0
RL: RCT (Reactant); RACT (Reactant or reagent)
(complex formation; palladium-catalyzed **arylation** of ketones by aryl halides using sterically hindered chelating ligands)

IT 199390-35-7P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(intermediate complex; palladium-catalyzed **arylation** of ketones by aryl halides using sterically hindered chelating ligands)

IT 451-40-1P, 1,2-Diphenylethanone 2042-85-5P, 1,2-Diphenyl-1-propanone 5033-67-0P, 2-(2-Methylphenyl)-1-phenylethanone 6721-67-1P, 3,3-Dimethyl-1-phenyl-2-butanone 13196-28-6P, 2-Phenyl-1-(2-thienyl)ethanone 13740-70-0P, 2-Methyl-1,2-diphenyl-1-propanone 24845-40-7P, 2-(4-Methoxyphenyl)-1-phenylethanone 27798-41-0P, 2-[4-(1,1-Dimethylethyl)phenyl]-1-phenylethanone 62043-83-8P, 3-(2-Oxo-2-phenylethyl)benzonitrile 86607-65-0P, 1-(2-Furanyl)-2-phenylethanone 93304-03-1P
RL: SPN (Synthetic preparation); PREP (Preparation)

CAS ONLINE PRINTOUT

(product; palladium-catalyzed **arylation** of ketones by aryl halides using sterically hindered chelating ligands)

IT 75-97-8, 3,3-Dimethyl-2-butanone 88-15-3, 2-Acetylthiophene 93-55-0, Propiophenone 95-46-5, 1-Bromo-2-methylbenzene 98-86-2, Acetophenone, reactions 104-92-7, 1-Bromo-4-methoxybenzene 108-86-1, Bromobenzene, reactions 591-50-4, Iodobenzene 611-70-1, Isobutyrophenone 932-16-1, 2-Acetyl-1-methylpyrrole 1192-62-7, 2-Acetyl furan 3972-65-4, 1-Bromo-4-(1,1-dimethyl ethyl)benzene 6952-59-6, 3-Bromobenzonitrile

RL: RCT (Reactant); RACT (Reactant or reagent)

(reactant; palladium-catalyzed **arylation** of ketones by aryl halides using sterically hindered chelating ligands)

L7 ANSWER 8 OF 8 CAPLUS COPYRIGHT 2002 ACS

AN 1995:764070 CAPLUS

DN 123:159350

TI Multiple Bonds between **Transition Metals** and Main-Group Elements. 145. Coordination Chemistry of Dirhenium Heptaoxide: Covalent Adducts and "Ionic Perrhenyl-Perrhenates"

AU Herrmann, Wolfgang A.; Roesky, Peter W.; Kuehn, Fritz E.; Elison, Martina; Artus, Georg; Scherer, Wolfgang; Romao, Carlos C.; Lopes, Andre; Basset, Jean-Marie

CS Anorganisch-chemisches Institut, Technischen Universitaet Muenchen, Garching, D-85747, Germany

SO Inorganic Chemistry (1995), 34(19), 4701-7

CODEN: INOCAJ; ISSN: 0020-1669

PB American Chemical Society

DT Journal

LA English

AB Dirhenium heptaoxide dissolves in donor solvents such as 1,2-dimethoxyethane (dme), THF, and MeCN to form adducts O₃ReOReO₃.cntdot.2L (L = monodentate ligand site). A strong reactivity enhancement of Re₂O₇ for alkylation, **arylation**, and similar reactions follows from this unsym. Lewis-base coordination. The terminal and bridging oxygens equilibrate in soln. (170 NMR). These adducts exhibit unsym. bent O bridges in their solid state structures, e.g. O₃ReOReO₃.cntdot.dme (x-ray diffraction study; crystal data: space group P21/c, a 12.162(2), b 10.830(1), c 8.195(1) .ANG., .beta. 90.80(1).degree., Z = 4). With stronger, chelating N-donors L₂ such as 2,2'-bipyridine, N,N'-dicyclohexyl-1,4-diazabuta-1,3-diene, and 2,2'-bis(pyrazolyl)propane the Re₂O₇.cntdot.2L complexes have rigid asym. bridges even in soln. (170 NMR). Thermal decomprn. liberates Re₂O₇ (EI-MS) and the resp. ligand (EI-MS, TG-MS). With tridentate ligands L₃ like tris(pyrazolyl)methane, 1,4,7-triazacyclononane (tacn), N,N',N'''-trimethyl-1,4,7-triazacyclononane (tacn*), 1,4,7-trithiacyclononane (ttcn), the Re-O-Re bridge breaks with formation of the ionic perrhenates [ReO₃L₃]⁺[ReO₄]⁻. An example is the ionic [ReO₃(tacn*)]⁺[ReO₄]⁻, the structure of which compd. was detd. by x-ray diffraction (crystal data: space group P.hivin.1, a 7.389(2), b 9.143(2), c 1.2294(3) .ANG., .alpha. 83.68(2), .beta. 77.99(2), .gamma. 89.29(2).degree., Z = 2). Intermol. H bridging plays a major role in the crystal packing of the ionic perrhenates.

TI Multiple Bonds between **Transition Metals** and Main-Group Elements. 145. Coordination Chemistry of Dirhenium Heptaoxide: Covalent Adducts and "Ionic Perrhenyl-Perrhenates"

AB Dirhenium heptaoxide dissolves in donor solvents such as 1,2-dimethoxyethane (dme), THF, and MeCN to form adducts O₃ReOReO₃.cntdot.2L (L = monodentate ligand site). A strong reactivity enhancement of Re₂O₇ for alkylation, **arylation**, and similar reactions follows from this unsym. Lewis-base coordination. The terminal and bridging oxygens equilibrate in soln. (170 NMR). These adducts exhibit unsym. bent O bridges in their solid state structures, e.g. O₃ReOReO₃.cntdot.dme (x-ray diffraction study; crystal

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data: space group P21/c, a 12.162(2), b 10.830(1), c 8.195(1) .ANG., .beta. 90.80(1).degree., z = 4). With stronger, chelating N-donors L2 such as 2,2'-bipyridine, N,N'-dicyclohexyl-1,4-diazabuta-1,3-diene, and 2,2'-bis(pyrazolyl)propane the Re2O7.cntdot.2L complexes have rigid asym. bridges even in soln. (170 NMR). Thermal decompn. liberates Re2O7 (EI-MS) and the resp. ligand (EI-MS, TG-MS). With tridentate ligands L3 like tris(pyrazolyl)methane, 1,4,7-triazacyclononane (tacn), N,N',N''-trimethyl-1,4,7-triazacyclononane (tacn*), 1,4,7-trithiacyclononane (ttcn), the Re-O-Re bridge breaks with formation of the ionic perrhenates [ReO3L3]+[ReO4]-. An example is the ionic [ReO3(tacn*)]+[ReO4]-, the structure of which compd. was detd. by x-ray diffraction (crystal data: space group P.hivin.1, a 7.389(2), b 9.143(2), c 1.2294(3) .ANG., .alpha. 83.68(2), .beta. 77.99(2), .gamma. 89.29(2).degree., z = 2). Intermol. H bridging plays a major role in the crystal packing of the ionic perrhenates.

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